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This is a summary of results from a program aimed at studying the atomic structure of semiconductor surfaces using scanning tunneling microscopy (STM). The bulk of the research concerned the epitaxial growth of metals on the (111) and the (100) surfaces of silicon, with particular emphasis on the metals indium and gallium. The STM images provided structural information on all of the metal-induced surface reconstructions in these systems as well as information on the general behavior of the metals on the Si surface, yielding insight into metal mobility, the effect of stepped substrates, and the nucleation of metal growth on the surface.

In addition to the semiconductor surface work, there has been some studies of the epitaxial growth of metals on Au(111), and the surface structure of the high temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$.

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22a. NAME OF RESPONSIBLE INDIVIDUAL: R. G. Brandt, ONR Physics Division

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Edward L. Ginzton Laboratory
W. W. Hansen Laboratories of Physics
Stanford University
Stanford, California 94305

Scanning Tunneling Microscopy of Semiconductor Surfaces

Final Report

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April 1, 1987 - September 30, 1989

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C. F. Quate

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Scanning Tunneling Microscopy of Semiconductor Surfaces

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Abstract

This is a brief summary of the accomplishments of a three-year research program aimed at studying the atomic structure of semiconductor surfaces using scanning tunneling microscopy (STM). The bulk of the research concerned the epitaxial growth of metals on the (111) and the (100) surfaces of silicon, with particular emphasis on the metals indium and gallium, both of which are dopant materials used in Si MBE. The STM images provided new structural information on all of the metal-induced surface reconstructions observed in these systems. Furthermore, studying the surfaces as a function of metal coverage provided information on the general behavior of the metals on the Si surface, yielding insight into metal mobility, the effect of stepped substrates, and the nucleation of metal growth on the surface.

In addition to the semiconductor surface work, there has been some studies of both metals and superconductors. The particular high temperature superconductor studied was $Bi_2Sr_2CaCu_2O_{8+\delta}$. Atomic resolution images of the cleavage surface were obtained for the first time, and the nature of the incommensurate superstructure previously seen in diffraction measurements of the bulk crystal structure was clarified. The work on metals concerned the epitaxial growth of metals on the Au(111) surface. These experiments were carried out in an ultra-high vacuum STM that was built entirely during the contract period.

The primary goal of this research program has been to use scanning tunneling microscopy (STM) to study the atomic structure of semiconductor surfaces, with an emphasis placed on two different areas: the structure of the ordered surface reconstructions that arise when a metal is deposited on Si, and the general behavior of the metals on the surface, including nucleation and the effect of steps. For the great majority of these reconstructions, little or no prior structural information was available, and the STM images revealed enough of the general nature of each structure to constrain atomic models that could be proposed.

An additional goal of studying compound semiconductor surfaces was addressed in only a limited sense with imaging of cleavage faces of GaAs and InP. Imaging of the more technologically important GaAs(100) faces was unsuccessful due to lack of appropriate sample preparation capabilities. Nevertheless, some of the work of Ga on Si proved to be relevant to problems that arise in the growth of GaAs on the Si(100) surface, and the surface reconstructions observed in this system were analogous in some respects to the GaAs(100) surface.

Atomic resolution imaging was also used to study epitaxial growth metals on the Au(111) surface, and the cleavage face of the high temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$.

From the viewpoint of instrumental development, some enhancements were added to an existing STM/vacuum system. In addition, an entirely new STM/vacuum system was built under partial support of this contract. This new system was optimized for fast scan images and incorporated in situ sample and tip transfer. The metal epitaxy work was carried out in this second system.

Studies of Metal Induced Reconstructions of the Silicon Surface

Most of the work on metals on Si has focussed on group III metals (In,Ga). These metals are notable for inducing different surface reconstructions depending on the density of the metal on the surface. In addition, these metals are used as dopants in Si MBE growth, and it has been demonstrated that the kinetics of dopant incorporation and in particular the behavior of surface segregated dopant layers during growth depend on the details of the bonding and structure of the

metals on the surface. These in turn are the surface reconstructions that are the primary concern of our studies.

Specific scientific results are summarized as follows:

1) Behavior of In on the Si(111)7×7 Surface

For the indium/silicon(111) system, we have now identified five different surface reconstructions in the range of coverages below one monolayer (ML): adatom replacement in the native Si 7×7 pattern at less than 0.1 ML, the $\sqrt{3}\times\sqrt{3}$ structure at 0.3 ML, the $\sqrt{31}\times\sqrt{31}$ at 0.6 ML, and two phases, 4×1 and $\sqrt{7}\times\sqrt{3}$, coexisting between 0.75 and 1 ML. The behavior at low coverage is of particular interest since the bonding arrangement of the In adatoms in either the 7×7 or the $\sqrt{3}\times\sqrt{3}$ structures is directly identified in the STM images. As mentioned previously, the determination of the metal atom bonding site in the $\sqrt{3}\times\sqrt{3}$ arrangement makes this the first metal induced reconstruction to have a detailed atomic structural model that is understood on both an experimental and theoretical basis. The In atoms lie on the threefold sites above second layer Si atoms, a location referred to as T_4 in recent literature. This result confirms a theoretical prediction that this is the lowest energy site for a group-III metal adatom in the $\sqrt{3}\times\sqrt{3}$ arrangement.

2) Ga Induced Reconstructions of Si(111)

The STM images show that up to 0.7 ML coverage, there are two new surface phases that occur. At low coverage, the behavior of Ga is identical to In, with Ga adatom replacement in the native 7×7 structure. The first new phase is at 1/3 ML which is the $\sqrt{3}\times\sqrt{3}$ reconstruction. The STM images confirm the same structure and metal bonding site as in In/Si(111). At higher coverage, a new incommensurate phase is seen which corresponds to a 6.3 x 6.3 RHEED pattern reported in the literature. This high coverage phase consists of well-ordered triangular subunits arranged in a quasi-periodic manner across the surface. The structure within the sub-units appears to be 1x1, in registry in the bulk Si lattice positions.

3) Behavior of Sub-monolayers of Sn on Si(111)

The structure of different reconstructions of tin on Si(111) has been studied. Tin (Sn) is of interest because it has been shown to grow with some degree of epitaxy on both Ge and Si substrates. Since Sn is just below Si and Ge in the periodic table, it might be expected that the surface reconstructions induced by Sn on Si might be very similar to those of clean Si or Ge. It has been demonstrated that a "normal" 7×7 structure can exist on Sn/Ge alloys. However, we find that deposition of Sn on Si produces new structures that are not seen on bare Si. For less than a monolayer (ML) of Sn, three different reconstructions are seen with 7×7, $\sqrt{3}\times\sqrt{3}$, and $2\sqrt{3}\times2\sqrt{3}$ periodicities. The 7×7 structure has the same unit cell as that of the clean surface but there is obvious disruption of the adatom structure. The $\sqrt{3}\times\sqrt{3}$ phase is a 1/3 ML array of adatoms similar to that of Al, Ga, or In on Si(111). The registration of adatoms at 7×7 / $\sqrt{3}\times\sqrt{3}$ phase boundaries indicates that the adatoms in the $\sqrt{3}\times\sqrt{3}$ structure lie in the threefold sites above second layer Si atoms. The $2\sqrt{3}\times2\sqrt{3}$ structure is shown to be two-fold symmetric with the three orientations on the surface giving the threefold symmetry apparent in the LEED pattern. All three surface phases are shown to coexist above 0.3 ML. Adatom trimers are seen on some 7×7 unit cells, suggesting a new structure that may be a prelude to the formation of the $\sqrt{3}\times\sqrt{3}$ phase.

4) Ga on Si(100)

This system is of particular interest because of the relevance to heteroepitaxial growth of GaAs on Si(001). Although most GaAs growth starts with a surface terminated by As rather than Ga, it has been shown that the behavior of Ga on the surface is crucial in the nucleation of growth on the surface. In addition it has been demonstrated that a Ga predeposition procedure can influence GaAs island size distribution in thin, discontinuous GaAs films. Control of the initial stages of growth is important because defects that form from the beginning, such as anti-phase domains, can propagate through the GaAs film and have a strong effect on its bulk

properties. The work on Ga/Si(100) can be subdivided into three areas: low coverage results, reconstructions at higher coverages, and the behavior of Ga on vicinal Si(100) surfaces.

At extremely low metal coverages, less than 0.1 monolayers (ML), the effects of the substrate surface are strongest, and the nucleation of growth can be studied in some detail. The Ga atoms are much more mobile than on the Si(111) surface under the same conditions. At low metal density (0.07 ML), the Ga atoms have a strong tendency to order in rows on the surface, parallel to the Si dimerization direction. As a result, areas covered by Ga are strongly elongated in <110> type directions. As the metal density is increased, these rows form local areas of 3×2 order. Where a step is present, metal growth tends to nucleate on the lower terrace edge, but is not necessarily confined to areas near the step. In general, neither steps nor defects on the substrate appear to play a strong role in controlling nucleation. In reference to the subsequent results on vicinal surfaces, it should be noted that the steps here were single-height whereas the interaction of Ga with double height steps is different.

The various ordered surface reconstructions of Ga on Si(100) up to 1 ML have also been studied. Below 0.5 ML, the Ga atoms form dimers that bond to the Si dimers, with the Ga dimers forming rows as was seen at low coverages. The Ga dimer rows form areas of 2x3 order up to 0.3 ML, and 2x2 order at 0.5 ML, in agreement with LEED data. All surface dangling bonds are saturated at 0.5 ML and so a different bonding behavior is expected above 0.5 ML. For such coverages, STM gives evidence for Ga growth on the 2x2 Ga terminated surface with an (nx8) ordering, where n is usually 4 or 5. The detailed nature of the reconstruction is not clear from the images, but it does not appear to involve Ga dimers.

The behavior of sub-monolayer coverages of Ga on vicinal (stepped) Si(100) surfaces has also been studied. Substrates were cut at 4° towards the (011) direction, resulting in a near-single-domain surface with double height steps spaced an average of 39Å (≈10 unit cells) apart. Growth on such single-domain surfaces has been proposed as one method to eliminate the formation of anti-phase domains during GaAs on Si growth. At room temperature, low coverages of deposited Ga do not disrupt the Si surface. The Ga atoms

appear to lie on the existing Si dimers, appearing as bright features in the STM images, just as seen on unstepped or single-stepped surfaces. However, if the sample is annealed after Ga deposition, there is significant disruption of the double-height step structure. At low coverages (<0.1 monolayer) the degree of disorder along the step edges appears to correlate with the amount of Ga on the surface. The double-height steps become kinked, or split into single height steps. Up to 0.1 monolayer no clear evidence of Ga growth on top of the Si dimers is observed, either at step edges or on the flat terraces. Rows and arrays of Ga are seen at higher coverages. Comparison of these results with the earlier work on untilted Si(100) shows that Ga is more reactive at double height steps than at single height steps. These results would imply that the effects of a Ga predeposition during GaAs growth on Si would be particularly pronounced on such vicinal surfaces.

The Surface Structure of the High Temperature Superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$

Real-space images with atomic resolution of the Bi-O place of $Bi_2Sr_2CaCu_2O_{8+\delta}$ were obtained for the first time by STM. Single-crystal samples were cleaved and imaged under UHV conditions at room temperature. The images clearly show the one-dimensional incommensurate superstructure along the **b**-axis that is common to this phase. High-resolution images show the positions of Bi atoms, revealing the structural nature of the superlattice. A missing row of Bi atoms occurs either every nine or ten atomic sites in both <110> directions, accounting for the measured incommensurate periodicity. Measured displacements of the atomic positions in both the **a** and **c**-axis directions show good agreement with X-ray measurements of the bulk structure.

Epitaxial Growth of Metals on the Au(111) Surface

We have studied the epitaxial growth of both Au and Ag on the Au(111) surface. Au(111) is unique among the closed packed surfaces of fcc metals since it exhibits a 22x1 reconstruction. It is interesting to compare and contrast the different behavior of Au and Ag growth on this surface,

both in terms of the different mobilities of the metals and the different responses of the growth to the reconstruction on the surface.

We have studied autoepitaxy on Au(111) from submonolayer up to 20 ML coverage at room temperature. At low coverages, the deposited Au nucleates into single layer clusters, with some correlation between cluster positions and domain boundaries in the 22x1 reconstruction. As the metal coverage increases, cluster coalescence by growth is observed. Cluster size distributions and spatial correlation functions have been extracted from the STM data. Higher layers start forming before the lower ones are completely filled. The number of incomplete layers increases with deposition rate and total thickness of the film. Room temperature diffusion smooths the terrace structure over a period of several hours. This process can be accelerated by a moderate anneal.

The growth of Ag on Au(111) is qualitatively similar to that of Au, and can be roughly described as layer by layer. The higher mobility of Ag produces smoother surfaces than Au. However, there is a significant difference in the growth of the first layer. At sub-monolayer coverages, Ag grows in fingers that are locked to the 22x1 reconstruction. The first Ag monolayer removes the reconstruction, and the growth is isotropic in further layers.

An entirely new STM and vacuum system was built in order to do the metals work. The vacuum chamber has facilities for in situ deposition of metals, as well as the annealing of samples up to several hundred degrees C. The design of the STM itself was based on compact instruments that had been built for use in air, with a simple mechanical drive for the tip to sample approach. One unique feature of the instrument is the integration of the tip, PZT scanner, and current preamplifier into an interchangeable cassette that plugs into the microscope. The ability to interchange tips in situ proved important for the Au work since the presence of relatively mobile Au atoms on the W tip often affected the stability of the tunneling. Electronics and software developed for this instrument have the capability of doing spectroscopic measurements in a variety of modes.

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